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LIGNITE HUMIC ACIDS AGGREGATES STUDIED BY HIGH RESOLUTION ULTRASONIC SPECTROSCOPY

Thermodynamic stability and molecular feature

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The thermodynamic stability of lignite humic acids (sodium salt) aggregates was studied by high resolution ultrasonic spectroscopy within the temperature interval from 5 to 90°C. The changes in differential ultrasonic velocity (U12) showed strong differences among humic solutions within the concentration range from 0.005 to 10 g L^{-1}. Measurement revealed several transitions which were attributed to the weakening of humic secondary structure. Concentration around 1 g L^{-1} seemed to be a limit under which the change of the prevalence and importance of hydration occurred. Above this concentration the difference in U12 decreased following the temperature increase which was explained as a dominance of hydrophilic hydration. In contrast, below this concentration, the temperature dependence of U12 resulted in increasing tendency which was attributed to the prevalence of hydrophobic hydration, i.e. uncovering of apolar groups towards surrounding water. Additional experiments in which the humic sample was modified by hydrochloric acid resulted in a slight structural stabilization which lead to the conclusion that humic micelle-like subaggregates form an open-layer assemblies easily accessible for interaction with an extraneous molecule. That was partly verified by addition of propionic acid which brought about even larger reconformation of humic aggregates and exhibition of polar groups towards hydration water.

The reversible changes in humate solutions induced by elevated temperatures provided the evidence about the existence of significant physical interactions among humic molecules resulting in formation of various kinds of aggregates. The nature of aggregates, mainly the stability and conformation, strongly depends on the concentration. Evidently, the changes observed in this work cannot be simply explained as expansions or conformational changes of macromolecular coils.

Keywords: *aggregation, hydrophilic hydration, hydrophobic hydration, lignite humic acids, stability, ultrasonic spectroscopy*

Introduction

The importance of humic substances for the sustainability of life on the Earth is well recognized. Despite the long-time study and important achievements in the identification of primary chemical composition, there is still lack of information on their physical structure. It is a consequence of way of humic substances formation, i.e. microbial decay of dead plant tissues and animal bodies and likely abiotic transformation promoted and modified by environmental conditions. Thereby they can be visualized as a highly complicated mixture of both aliphatic and aromatic molecules forming unique and versatile structures [1].

A number of studies give excellent accounts of the present state of knowledge regarding the secondary structure of humic substances. It is generally recognized that humic molecules are surface-active and can solubilize a wide variety of hydrophobic species [2–4]. This behavior of humic molecules is usually attributed to their micelle-like organizations in aqueous solutions. However, high concentrations required for the formation of such structures rarely correspond to environmental situations [4]. It is therefore of practical interest to study the character of humic organizations also in diluted solutions. In fact, the solubilization capacity of humic substances has been reported also at significantly lower concentration than the critical micelle concentration reported for humic substances (i.e. from 2–10 g L^{-1}). Wershaw [5] proposed two possible explanations: (i) partition of hydrophobic molecules into interiors of aggregates of amphiphilic molecules at concentrations lower than the critical micelle concentration (premicellar aggregates), or (ii) association of hydrophobic molecules with the non-polar parts of unassociated amphiphilic molecules. Evidence for micelle-like organizations which does not feature a critical micelle concentration was found by Engebretson *et al.* [6, 7]. A decade ago, spectroscopic evidence for existence of humic pseudomicelles was reviewed [8]. It has been stated that the prevailing interactions holding humic aggregates/molecules together in diluted solutions are in particular hydrophobic weak interactions. Micelle-like character of humic molecules indicates the hydrophobic-hydrophilic nature of molecules and implies presence of charged sites at neutral pH. Those are in diluted solutions separated due to repulsive forces and the conditions for H-bridges formation are limited.

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Nowadays there is a major disagreement about the conformational structure of humic constituents. The several proposed structural formulas consist mainly of highly condensed aromatic rings substituted with carboxylic, phenolic and methoxy groups [9]. The most frequently adopted view is that humic constituents in solutions are polymers which coil at high concentrations, low acidity and high ionic strength, but become linear in neutral solutions, at low ionic strength and low concentration [10].

Piccolo *et al*. [1] has presented an extended theory, that instead of viewing HA as stable polymers, humic constituents should be considered as supramolecular associations of relatively small heterogeneous molecules held together by weak dispersive forces such as van der Waals, π–π, CH–π interactions and H-bonds. This conclusion was based on the large-scale experimental data showing that after modification of the original humic-solute mixtures, the macroscopic dimension of this supramolecular association was disrupted in smaller sized associations with reduced chemical complexity. The disruption by acid was attributed to the formation of new, preferably intermolecular, hydrogen bonds. Recent experiment also brought the evidence of prevailing hydrophobic interactions holding together humic aggregates in diluted solutions [11]. Further, when the distance among different humic components was reduced due to an increase in concentration, the negatively charged sites, present at pH 7, produced an electrostatic repulsion that overcame the hydrophobic aggregation forces. As a result, the dimension of humic association decreased.

In addition, recent results obtained by the high resolution ultrasonic spectroscopy (HRUS) indicated that the humic aggregation instead of being described as a micellization should be better viewed as a kind of hydrotropy process [12]. According to theory of hydrotropy, small molecules, with hydrophobic chains shorter than eight carbons, tend to self-aggregate at concentrations sometimes significantly lower than the critical micelle concentration reported for surfactants.

Most methods which can be applied to elucidate the secondary structure of humic substances have several limitations, such as composition of mobile phase for the applications of size exclusion chromatography or concentration of humic solutions limitating a large number of spectroscopic methods. Such limitations can be overcome by a recently developed analytical technique, the high resolution ultrasonic spectroscopy (HRUS), measuring the velocity and attenuation of ultrasonic wave propagating through the liquid sample. In principle the ultrasonic wave interacts with the sample's interior, causes its compression and decompression and thereby enables the analysis of its physical and chemical properties including the information on both inter- and intramolecular nature of molecular organizations and their hydration [13]. One of the advantages of that method is a bimodal arrangement when the sample properties can be monitored either under isothermal conditions or under non-isothermal regime [14].

The purpose of this work was to monitor changes in ultrasonic parameters (ultrasonic velocity) induced by heating of HA solutions at different concentrations, covering the range from 10 to 0.005 g L^{-1}. The conformational rearrangement of secondary structure of humic molecules was further evaluated upon addition of selected modifiers to humic solutions.

Experimental

Humic substances

Humic acids (HA) (a part of humic substances soluble in alkali media) were isolated from the South Moravian lignite collected from the Mír mine in the area of Mikulčice, near Hodonín, Moravia, the Czech Republic [15] using standard alkali extraction with 0.5 mol L^{-1} NaOH and 0.1 mol L^{-1} $Na_4P_2O_7$. Full details on the extraction procedure and HA characterization can be found elsewhere [16–20]. The ash content was approximately 2%.

HA sample was titrated to pH 7 by 0.1 mol L^{-1} NaOH employing an automatic titrator (Schott, TitroLine Alpha Plus) under constant stirring. After reaching the constant value for 60 min, the sodium humate (NaHA) solution was filtered, freezed and lyophilized. The product was milled in an agate mortar and stored. Details on the elemental and composition analysis of HA sample are given in [12–19].

HRUS measurement

To monitor ultrasonic velocity and attenuation, HRUS 102 device (Ultrasonic-Scientific, Dublin, Ireland) was employed. HRUS consists of two independent quartz cells termostated by a water bath; cell 1 serves as a sample cell and cell 2 as a reference. All settings up were carried at 25.00±0.02°C, under constant stirring (600 rpm) and at ultrasound frequency of 5480 kHz.

NaHA was dissolved in deionized water to desired concentration in the range of 0.005 to 10 g L^{-1}. Cell 1 was loaded up by 1 mL of a sample whereas cell 2 by 1 mL of deionized water.

Thermal behaviour of NaHA solutions was investigated using following temperature regime: step 1 – from 25 to 90°C, back to 5°C; step 2 – from 5 to 90°C and back to 5°C; step 3 – from 5 to 90°C and back to 25°C. Heating and cooling rate were constant 0.35°C min^{-1}.

Then the influence of adding HCl and propionic acid was tested. The sample of concentration of 1 g L^{-1} was modified by the addition of HCl or propionic acid to obtain pH 3.5. The temperature regime was the same as for original sample. The amount of added compounds was in the comparison with the amount of HAs negligible and therefore the ionic strength of the solution has been changed only infinitesimally.

Difference between cells 1 and 2, i.e. U12 was measured. For ultrasonic velocity the resolution of the spectrometer is below 10^{-5}%. All experiments were carried out in duplicate and no significant deviations between experimental results have been observed. Obtained results were smoothed and plotted against the temperature (reported figures).

Results and discussion

Influence of concentration

The velocity of sound is extremely sensitive to temperature variations. In fact, with increasing temperature there is a significant increase of velocity up to 74°C while above that temperature a slow decrease. At low temperatures both compressibility and density of water are high, causing a lower velocity of sound. As the temperature increases the compressibility goes through a minimum whereas the density goes through a maximum. Combination of these two properties leads to the maximum in the velocity of sound [21].

To avoid the influence of such anomalies in the present work, results are given as a difference of ultrasonic velocity (U12). An example of temperature dependence in the whole temperature regime is given in Fig. 1 (sample 1 g L^{-1}). One can see that the changes induced by elevated temperatures from 5 to 90°C were reversible which implies that processes were rather of physical than chemical character. The only exception is a shift in U12 to lower values for the second cycle in comparison with the first one. That can be attributed to additional dissolution of humic molecules in the solvent.

The first heating cycle (0 to 420 min in Fig. 1) was used to adjust humic samples having the same 'thermal history', mainly to be completely dissolved since such processes in humic solutions can be rather slow [22]. The first part of second heating cycle (from 420 to 660 min, Fig. 1), has been used for monitoring the changes in humic solutions induced by heat while the third one for checking the reproducibility of the experiment.

Figures 2–4 report example of temperature dependence of ultrasonic velocity difference of humic solution within concentration range 0.005–10 g L^{-1}. As can be seen the temperature dependence of differential ultrasonic velocity dramatically changes with changing HA concentration. Concentration of 10 g L^{-1} (Fig. 2) showed a monotonous exponential decay. The exception in monotonous decrease can be seen at low temperature up to 8°C. This artifact was observed during each heating cycle including low concentrations and it can be attributed to the switch in temperature program from cooling to heating ramp. Therefore, in further considerations it is not taken into account.

For incompressible systems, the dependence of U12 on temperature linearly decreases for most hydrophilic materials, which is a result of the decrease in storage modulus of water with temperature [23, 24]. Such a linear decrease is associated with the decrease in dielectric constant of water causing a decrease in the strength of water H-bonds which is the main driving force assembling the humic molecules/aggregates together. The water in close vicinity of solute molecules (water shell) has been reported to be more supportive for ultrasonic wave propagation [24, 25] since it is (among others) 10–20% denser than the bulk water [26]. The exponential-like decrease shown in Fig. 2 can be explained by the fact that the strength of the attractive hydrophobic interactions among aggregating humic molecules slightly increases with temperature. A shorter distance between

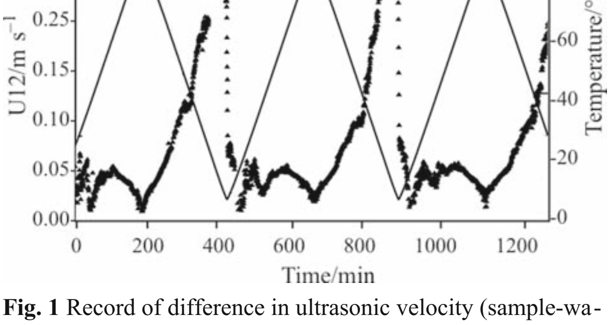

Fig. 1 Record of difference in ultrasonic velocity (sample-water, U12) and temperature program for lignite humate solution 1 g L^{-1}. Demonstration of reversibility and reproducibility of obtained results

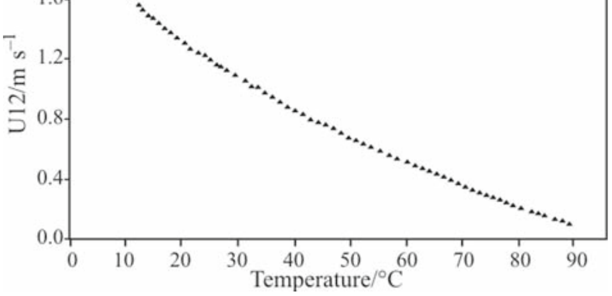

Fig. 2 Difference in ultrasonic velocity (sample-water, U12) for 10 g L^{-1} lignite humate sample

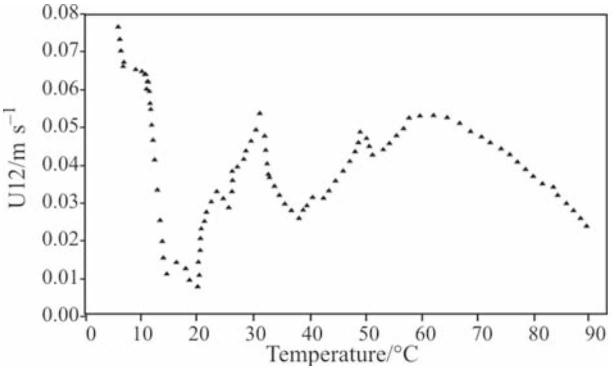

Fig. 3 Difference in ultrasonic velocity (sample-water, U12) for 1 g L^{-1} lignite humate sample

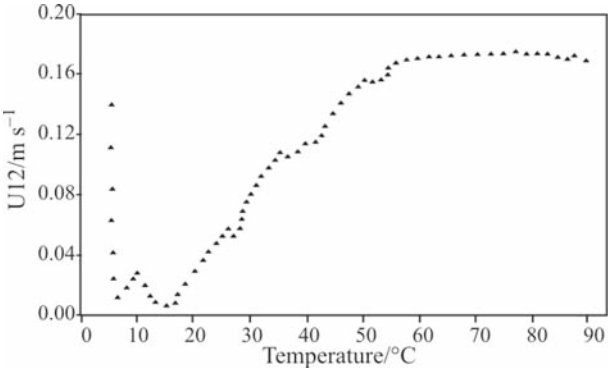

Fig. 4 Difference in ultrasonic velocity (sample-water, U12) for 0.005 g L^{-1} lignite humate sample

humic molecules in aggregates with increasing temperature causes its higher density, supports the elastic response of compression and decrease the relaxation time of a compressed hydrophobic structure. In addition, a decrease in mutual repulsion of charged head-groups induced by elevated temperature can be expected as well [27].

Progressive dilution of investigated solutions brought about weakening of humic secondary structure. It can be identified in Fig. 3 where concentration 1 g L^{-1} is reported. One can see several breaks indicating transitions which can be attributed to the unfolding and disruption of humic aggregates [23, 24, 28, 29]. In principal, an increase in velocity indicates the hydration changes, namely processes of unfolding or aggregate decomposition while decrease is usually associated with increase in intrinsic compressibility or intra-molecular 'melting' without significant unfolding [23]. Basically, the concentration decrease was associated with the shift of transition temperature to lower values; simultaneously, the number and 'intensity' of transitions increased. It seems that there is a lower number and/or strength of weak interactions stabilizing aggregates in diluted humic solutions. Such observation partly verifies conclusions reported in [11].

It is noteworthy that concentration 1 g L^{-1} represents a limit concentration. Whereas there is still the shift of transition temperatures to lower values with progressive dilution (reflecting the gradual destabilization) there is a remarkable change in the slope of dependency. It can be identified in the representative record for concentration 0.005 g L^{-1} (Fig. 4). Since the ultrasonic velocity depends on the state of water in the hydration shell [25], evidently, there is a different affinity of water in hydration shell to humic molecules. Therefore we assume that such behavior is caused by the reduction in the polarity of surface of humic aggregates. Those are not perfectly hydrated any longer under 1 g L^{-1} and switched mostly into so-called hydrophobic hydration. Indeed, the contribution of highly hydrated atomic groups would increase U12, the contribution of hydrophobic hydration is close to zero. It is well known that hydrophobic hydration produces a reduction in density of hydrating water shell [30] and an increase in the heat capacity [31]. Due to the decrease in dipole moment of water molecules at elevated temperatures, hydrophobic hydration behaves in an opposite manner to polar hydration. As a result, the increase in U12 parameter can be seen under concentration 1 g L^{-1}.

This conclusion is in contrast with results of Palmer and von Wandruszka [32] who used dynamic light scattering for evaluation of hydrodynamic diameter of humic and fulvic acids at elevated temperatures. The concentrations of measured samples were in the range 0.01–0.03 g L^{-1}. In most cases the obtained results indicated the increase in hydrodynamic diameter mainly in the temperature range 10–40°C which has been attributed to heat-induced phase separation known as clouding effect observed frequently for non-ionic surfactants. In the light of our observations, it seems that elevated temperatures increase also the density of hydration shell around hydrophobic molecules/aggregates which can be interpreted as an enlargement of humic aggregate dimensions, or better of hydrodynamic dimension. However, humic acids generally consist of a huge number of molecules possessing different polarity and polarizability, thus, the temperature induced aggregation promoted by weakening of hydration shell around hydrophilic moieties can not be excluded.

Modified humic solutions

The Piccolo humic theory of supramolecular arrangement of relatively small heterogeneous molecules [1] was experimentally supported by the large-scale experimental data obtained by Size Exclusion Chromatography. After addition of modifiers such as natural organic acids, e.g., propionic acid, to the original humic-solute mixture, the macroscopic dimension of this supramolecular association was disrupted in smaller sized associations with reduced chemical complexity. This disruption by organic acid additions was attributed to the formation of new inter-molecular hydrogen bonds which are thermodynamically more stable than the hydrophobic interactions stabilizing humic conformations at neutral conditions. The theoretical and qualitative interpretations of the above self-association/self-aggregation theory was strongly criticized [33], nevertheless, the theory has gained the growing interest and recent experiments brought new evidences [9, 12, 34–36].

To test that view as well as our previous assumptions [12], 1 g L^{-1} humic solution was treated by propionic and hydrochloric acids (decrease in pH from 7 to 3.5) to observe changes in stability induced by protonization of COOH groups and consequently a change in the stability of humate aggregates. It is important to note that the amount of additives was very low in comparison with the volume of humic solutions (microliters of additives to milliliters of humic acids). In addition water in the reference cell was modified by the same amount of modifiers as humic solution. Therefore, the changes in structure stability can be attributed only to the action of modifiers and the concentration and composition of humic solution remained practically constant.

Figure 5 reports the HRUS records of 1 g L^{-1} humate solution modified by hydrochloric acid. As demonstrated earlier such modification caused the protonization of humic molecules which decreases the strength of repulsive forces of charged sites and promotes the aggregation and formation of larger humic aggregates [1, 12]. Figure 5 shows that the modification had a slight effect on the stability of secondary humic structure, in fact temperatures of transitions were slightly shifted to higher values indicating the employment of higher number of weak bonds (probably H-bonds) stabilizing humic structure. Values of U12 are larger in modified sample which can indicate either better hydration or lower compressibility of resulted aggregates or a decrease in the relaxation time of present hydrophobic cores. Since the former is in contrast with enhanced capability of humic substances to interact with hydrophobic compounds at lower pH induced by hydrochloric acid [2], we suppose a slight modification of the compressibility of aggregates. The protonization of polar head-groups of molecules involved into such micelle-like structures lead to the decrease of their mutual repulsions which can, although only slightly, decrease the compressibility of the aggregates or influence the relaxation time [25]. Assuming the spherical geometry of a humic aggregate, polar head-groups represent a barrier for hydrophobic compound to interact with hydrophobic core. It invokes a view in which humic aggregates are arranged in planar structures or open-layer assemblies variably oriented in solutions. That is partly in line with recently proposed model of aggregation of humic acids based on their similarity with hydrotropic compounds [12]. The planar structure formed by some hydrotropic compounds is well recognized [37]. Moreover the strength of weak hydrophobic interactions strongly depends on their orientation [38] and repulsion of deprotonized polar groups at neutral pH maintains the structure unfolded. However, the hydrotropy model does not suit to humic self-assembly mechanisms perfectly since no mutual stacking among aromatic hydrotropic molecules is supposed [36], while that is probable in case of highly heterogeneous humic mixture [1, 20].

In contrast to hydrochloric acid, addition of propionic acid into humic sample gave a completely different result (Fig. 6). All the temperatures of break registered in non-treated sample were either shifted to higher temperatures, diminished or even disappeared. The slope of the record is similar to those at higher concentrations. Therefore, it is clear that propionic acid action caused a more intense stabilization effect towards aggregates associated with the increase in number of H-bonds and probably reaggregation of secondary structure [12].

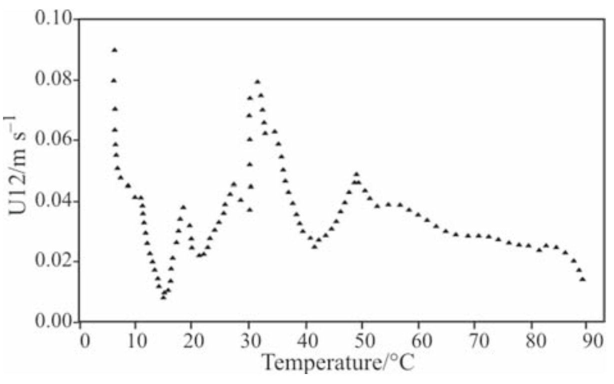

Fig. 5 Difference in ultrasonic velocity (sample-water, U12) for 1 g L^{-1} lignite humate, sample modified by HCl from pH 7 to 3.5

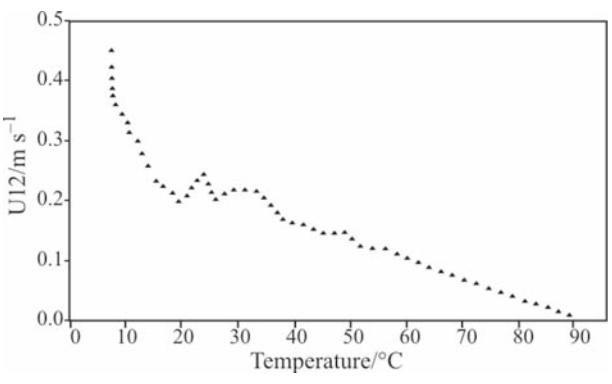

Fig. 6 Difference in ultrasonic velocity (sample-water, U12) for 1 g L^{-1} lignite humate, sample modified by propionic acid from pH 7 to 3.5

In the light of above-discussion, the slope of the dependence, if compared with the non-treated sample, indicates the prevalence of hydrophilic hydration. It cannot be also excluded the hypothesis that humic hydrophobic molecules were separated from each and surrounded by propionic acids molecules. That phenomenon again reflects the consequences of the effect of hydrotropy [39]. In this case, water shell surrounds the polar part of propionic acid while hydrophobic is oriented towards humic molecules. Due to H-bridging between propionic acid and water, such arrangement is more thermodynamically stable and enhances the solubilization of hydrophobic humic molecules. Organic acids represent a major pool of plant root exudates and are able to dissociate humic supramolecular structure present in rhizosphere into smaller fractions which may deliver bio-active molecules to plants or activate stimulation mechanisms [1, 40]. It has been found, that the most active, from biological point of view, are hydrophilic components [40]. Since presence of organic acid changed the hydration shell of humic aggregates from hydrophobic to hydrophilic, due to hydrotropy, the exudates can provide a hydrophilic shuttle allowing to humic aggregates to penetrate the cell wall and incorporate into the Krebs cycle.

Conclusions

The thermodynamic stability of lignite humic acids (sodium salts) aggregates was studied by high resolution ultrasonic spectroscopy within the temperature interval from 5 to 90°C. The changes in differential ultrasonic velocity (U12) showed strong differences among humic solutions within the concentration range from 0.005 to 10 g L^{-1}. Records showed several transitions which were attributed to the weakening of humic structure caused by decreasing number of stabilizing weak interactions. Concentration around 1 g L^{-1} seemed to be a limit under which the prevalence and importance of hydration dramatically changed. Above this concentration the difference in ultrasonic velocity decreased following the temperature increase which was explained as dominance of hydrophilic hydration. In contrast, below this concentration, the temperature dependence of U12 exhibited increasing tendency which was attributed to the prevalence of hydrophobic hydration, i.e. uncovering of apolar groups towards surrounding water.

Additional experiments in which the 1 g L^{-1} concentrated sample was modified by hydrochloric acid resulted in a slight stabilization which lead to the conclusion that humic micelle-like sub-aggregates form an open-layer assemblies easily accessible for extraneous molecules. That was partly verified by addition of propionic acid which brought about even larger reconformation of humic aggregates and exhibition of polar groups towards hydration water. It is very important knowledge, since such interaction can play role in biological processes occurring in rhizosphere and can be technologically used to boost fertility of agricultural soils as well as to enhance the efficiency of organic fertilizers.

The reversible changes in humate solutions induced by heat provided the evidence about the existence of significant physical interactions among humic molecules resulting in formation of various sorts of aggregates. The nature of aggregates, mainly stability and conformation strongly depends on the concentration. Evidently, the changes observed in this work cannot be simply explained as expansions or conformational changes of macromolecular coils.

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